Anharmonicity and Quantum Effect in Thermal Expansion of an Invar Alloy

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Introduction: Thermal expansion of Invar alloy

1897 C. E. Guillaume
1920 Nobel Prize Physics


**fcc FeNi alloy**

- 36Invar $\text{Fe}_{64.6}\text{Ni}_{35.4}$
- 42Invar $\text{Fe}_{58}\text{Ni}_{42}$
- Kovar $\text{Fe}_{54}\text{Ni}_{29}\text{Co}_{17}$
- 45Permalloy $\text{Fe}_{55}\text{Ni}_{45}$
- Inconel $\text{Fe}_{28}\text{Ni}_{72}$
- 78Permalloy $\text{Fe}_{22}\text{Ni}_{78}$

Weiss high-spin & low-spin model


Weiss high-spin & low-spin model

- HS more stable, longer distance
- LS more unstable, shorter distance

Higher $T$, larger LS concentration

Compensate for normal thermal expansion

Almost no thermal expansion from 0 to 400 K
Purpose of this work

1. Thermal expansion originates from thermal vibration Quantum effect at LT?

2. Transformation of HS ⇔ LS only in Fe atoms Local thermal expansion especially around Ni?

3. Anharmonicity without thermal expansion

Path-Integral Effective Classical Potential (PIECP) method

EXAFS & PIECP

Normal thermal expansion originates from anharmonic interatomic potentials
Measurement & analysis of EXAFS

PF-PAC No. 2010G551
Beam time used: 48 hours

KEK-PF BL9C  Si(111)
Fe_{64.6}Ni_{35.4} foil (8 \mu m) commercial transmission mode
I_0 N_2 100%
I Ar 50% + N_2 50%

EXAFS function $k^3 \chi(k)$ and their Fourier transforms

\[ \chi(k) = \frac{N S_0^2}{kR^2} e^{-C_2 k^2} \sin 2kR + \phi(k) - \frac{4}{3} C_3 k^3 \]

Calibration of $T$

Mean square (cubic) relative displacements

Abs. distance
FEFF
Relative distance
Empirical
Path Integral Effective Classical Potential (PIECP)


Convenient quantum mechanical simulation method in anharmonic systems

Monte Carlo simulations

FeNi 500 atoms (125 fcc lattices)
Periodic conditions
Fe:Ni=64.6:35.4 random distribution
11 samples

Atomic potentials

Embedded Atom Method (EAM)
Empirical potentials for metals


Total energies using present EAM potentials

<table>
<thead>
<tr>
<th>System</th>
<th>State</th>
<th>(R_e (\text{Å}))</th>
<th>(E(R_e) \text{ (eV)})</th>
<th>Remark</th>
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</thead>
<tbody>
<tr>
<td>fcc Fe</td>
<td>HS</td>
<td>2.530</td>
<td>-4.292</td>
<td>LS more stable by 8 meV</td>
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<tr>
<td></td>
<td>LS</td>
<td>2.492</td>
<td>-4.300</td>
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<tr>
<td>fcc Fe_{65}Ni_{35}</td>
<td>HS</td>
<td>2.530</td>
<td>-4.388</td>
<td>HS more stable by 25 meV</td>
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<td>LS</td>
<td>2.504</td>
<td>-4.363</td>
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<tr>
<td>fcc Ni</td>
<td></td>
<td>2.490</td>
<td>-4.450</td>
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</table>
Results of thermal expansion by EXAFS analysis

Relative interatomic distance for the 1st & 3rd NN shells

Bond (interatomic) distance & lattice distance

\[ R_{\text{bond}} = R_{\text{lattice}} + \frac{<u_{\bot}^2>}{2R_{\text{lattice}}} \]

Vibration perpendicular to the bond

\[ <u_{\bot}^2> \text{ from } \Theta_D \]

Fe 1st NN: almost no thermal expansion
Ni 1st NN: smaller than fcc Ni
3rd NN: associated with lattice

MSRD for 1st & 3rd NN shells

\[ C_2 (10^{-2} \text{Å}^2) \]

\[ \Theta_D \]

Temperatures:
- \( \Theta_{\text{Cu}} = 331 \text{ K} \)
- \( \Theta_{\text{Ni}} = 409 \text{ K} \)
- \( \Theta_{\text{Invar}} = 430 \text{ K} \)
Computational results for thermal expansion

Quantum
Both bond & lattice distances agree well with experiments

Classical
At LT (<100 K) large expansion deviates from experiments at LT

Conclusion 1: Quantum effect
Very important at LT
Without quantum effect, normal thermal expansion
Analysis of each component in 1st NN shells

EXAFS cannot distinguish 1st NN Fe-Fe & Fe-Ni or Ni-Ni & Ni-Fe
PIECP MC can easily distinguish

To show hypothetical normal expansion, case of HS-only Fe was calculated (dashed lines)

Fe-Fe almost no thermal expansion
Large deviation from HS-only results that may show hypothetical normal thermal expansion

Ni-Fe, Ni-Ni smaller than normal due to change of Fe potential

Expansion of Ni-Fe larger than Ni-Ni
Fe surrounded by many Ni shows HS Ni-Ni potential softer
• Ni-Fe more likely to follow lattice

Conclusion 2: Local expansion
Ni also shows very small expansion due to the change of Fe potentials.
Asymmetry or anharmonicity

1st NN
Both Fe & Ni show rather normal $C_3$

Conclusion 3: Asymmetry in no thermal expansion system
Even in no thermal expansion system, RDF is asymmetric as usual
Anharmonicity exists normally

3rd NN
Both Fe & Ni show no asymmetry
No chemical bond in 3rd NN shell gives no anharmoninicity
RDF for non-interaction
From central limit theorem, RDF should be gaussian

Summary

Combining EXAFS & PIECP, thermal expansion of Invar alloy Fe$_{64.6}$Ni$_{35.4}$ is studied.

1. Thermal expansion originates from thermal vibration
   Quantum effect at low temperature?
   
   Quantum effect at LT is essential.
   Without quantum effect, normal thermal expansion

2. Transformation of HS ⇔ LS only in Fe
   Local thermal expansion especially around Ni?
   
   Fe 1$^{st}$ NN almost no expansion
   Ni 1$^{st}$ NN smaller expansion than normal
   due to Fe potentials

3. Anharmonicity in the no thermal expansion system
   
   Although thermal expansion inherently originates from anharmonicity, there can be clearly found the asymmetry of the RDF (=3$^{rd}$-order anharmonicity) even in the system without thermal expansion.